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Project: A 1.13
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Edgewood Arsenal, Md.

A MEMORANDUM REPORT

THE SYNTHESIS OF MCE, CYANO (DIMETHYLAMINO) ETHOXYPHOSPHINE OXIDE

by

Walter H. C. Rueggeberg. Capt., C.W.S.

T/3 Abram Ginsburg

October 8, 1945

[redacted]

11 Sept 45 E.H.S.
Date Initial
By Authority of C.G.
Edgewood Arsenal, Md.

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Project: A 1.13
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A Memorandum Report

The Synthesis of MCE, Cyano(dimethylamino)ethoxyphosphine Oxide

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By DOD DIR 5200.9

Walter H. C. Rueggeberg, Capt., C.W.S.
T/3 Abram Ginsburg

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ABSTRACT

OBJECT:

The object of Project A 1.13 is to investigate agent MCE and its analogs.

The object of the work described in this report was to develop a method of synthesis of MCE suitable for use in the pilot plant. The method is based upon that developed by the Germans.

RESULTS:

1. The 2-step synthesis of MCE, as described by the Germans,

$$(CH_3)_2NH\cdot HCl + POCl_3 \longrightarrow (CH_3)_2NPOCl_2 + 2HCl$$

$$(CH_3)_2NPOCl_2 + 2NaCN + C_2H_5OH \longrightarrow (CH_3)_2NPO(CN)(OC_2H_5) + 2NaCl + HCN$$

was investigated with the view of adaptation to pilot-plant operations.

2. Dimethylamine hydrochloride, a benzene solution of free dimethylamine, and gaseous dimethylamine were tried in the synthesis of the MCE intermediate (dimethylaminodichlorophosphine oxide), using various molar ratios of $POCl_3$ to the amine.

The molar ratios and reaction periods leading to best yields were found to be the following:

Material in First Column	$POCl_3$	Reaction Conditions		Yield
		Time	Temp.	
mols	mols	hr.	°C.	%
Dimethylamine hydrochloride 1.0	3.0	6	111.5	89.3
" 1.0	4.0	6.5	111	92.5
Dimethylamine (dissolved in benzene) 0.5	0.75	5	119	89.6
Gaseous dimethylamine* 2.2	4.4	6	121	90.1

* Only two runs were made using gaseous dimethylamine but the data obtained agreed well with those where a benzene solution of the amine was used.

Using a molar ratio of the amine less than that indicated above results in a considerable lowering of the yield of MCE intermediate.

3. Pure dimethylaminodichlorophosphine oxide was found to have the following physical properties:

$n_D^{20} = 1.4630$ [redacted]

Density at 20°C. = 1.363 g./ml.

b.p. = 81°C. at 14 mm.

b.p. = 120°C. at 77 mm.

[redacted]

4. By reacting 0.5[illegible] mol of distilled dimethylaminodichlorophosphine oxide with 1.42 mols of NaCN and 0.54 mol of ethanol in 90 ml. of either benzene or chlorobenzene, a yield of 80 to 81% of distilled MCE was obtained. The purest sample obtained was found to have the following characteristics:

n_D^{20} = 1.4240

Density at 20°C. = 1.080 g./ml.
b.p. = 72.5-73°C. at 1.5 mm.
b.p. = 86-87°C. at 3 mm.

5. By reacting 0.50 mol of distilled dimethylaminodichlorophosphine oxide with 1.42 mols of NaCN and 0.54 mol of ethanol in 90 ml. of benzene, followed by partial vacuum stripping of benzene, there remained 84.1 g. of partially stripped, undistilled MCE having the following approximate composition:

MCE	= 74.8%	n_D^{20} = 1.4291
MCE intermediate	= 3.2%	
Benzene and other inert material (by difference)	= 22.0%	d 25/4 = 1.082

6. One run was made in which all distillations other than stripping of excess reagents and solvents were avoided.

By reacting 64.6 g. of stripped, undistilled MCE intermediate with 1.42 mols of NaCN and 0.54 mol ethanol in 90 ml. of chlorobenzene, there was obtained after partial stripping of excess chlorobenzene, 69.2 g. of partially stripped MCE residue having the following approximate composition:

MCE	= 56.7%
MCE intermediate	= 0.1%
Chlorobenzene and other inert material (by difference)	= 43.2%

n_D^{20} = 1.4616

Density = 1.096 g./ml. at 25°C.

7. The crude MCE reaction product, after filtering, was found to contain about 3% of dissolved gaseous HCN.

8. The synthesis of MCE was found to be very susceptible to the presence of moisture. The presence of 1% of water in the ethanol used was found to lower the yield of distilled MCE from 80-81% to 54%.

Drying of the reagents by refluxing and removing H_2O as an azeotrope with either benzene or chlorobenzene was found to be effective.

CONCLUSIONS:

1. Dimethylaminodichlorophosphine oxide can be prepared in yields of about 90% from $POCl_3$ and either dimethylamine hydrochloride or the free dimethylamine.

2. The use of the free amine in the synthesis of dimethylaminodichlorophosphine oxide requires only 1.5 to 2 mols of $POCl_3$ per mol of amine whereas dimethylamine hydrochloride requires at least 3 mols of $POCl_3$ per mol of amine hydrochloride for comparable yields.

3. Under anhydrous conditions, the MCE intermediate will react with NaCN and ethanol in either benzene or chlorobenzene to produce about 80% of distilled MCE.

4. If distilled intermediate is used, merely stripping the MCE crude reaction products free of volatile matter will produce an acceptable grade of MCE in yields of about 78%.

5. Undistilled, stripped MCE intermediate can be used in the MCE synthesis, resulting, however, in somewhat lower yields and a product of inferior quality.

RECOMMENDATIONS:

It is recommended that:

1. In pilot plant operations, dimethylaminodichlorophosphine oxide (MCE intermediate) be prepared by the direct action of 1 mol of gaseous dimethylamine on 1.5 to 2 mols of $POCl_3$.

2. The MCE intermediate be distilled before its reaction with the other reagents to produce MCE is undertaken.

3. In view of the sensitivity of the MCE synthesis toward moisture and HCl all reagents be kept thoroughly anhydrous. The azeotropic removal of water with benzene or chlorobenzene (or with ethanol and benzene) is recommended prior to the addition of the MCE intermediate to the other reagents.

[redacted]

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The Synthesis of MCE, Cyano(dimethylamino)ethoxyphosphine Oxide

Project: A 1.13 T.D.M.R. 1183

I. INTRODUCTION.

A. Object.

The object of Project A 1.13 is to investigate agent MCE and its analogs.

The object of the work described in this report was to develop a method of synthesis of MCE suitable for use in the pilot plant. The method is based upon that developed by the Germans.

B. Authority.

Authority for this work is contained in Project A 1.13, MCE and Its Analogs, for the fiscal year 1946.

II. HISTORICAL.

Prior to the fall of Germany in May 1945, the only published data relative to compounds containing nitrogen-phosphorus linkages similar to that in MCE were those of Michaelis (Ann. 326, 179 ff, 1902). References have been made to the effect that the Russians and the Swedes were interested in the MCE type compound but no published data are available.

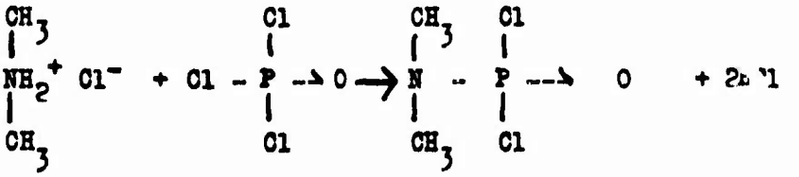
After the fall of Germany, the work on MCE in that country was made available through Intelligence Division Report No. 3709.

At the present time considerable work on MCE and its analogs is being conducted in the U.S.A. as well as in Great Britain.

III. THEORETICAL.

The synthesis of MCE (dimethylaminocyanoethoxyphosphine oxide) is a two-step process using $POCl_3$ and dimethylamine as its hydrochloride as starting materials. This process may be represented by the following equations:

Step 1



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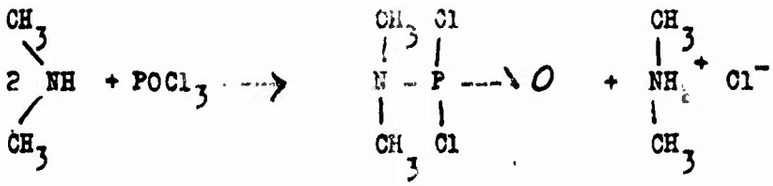
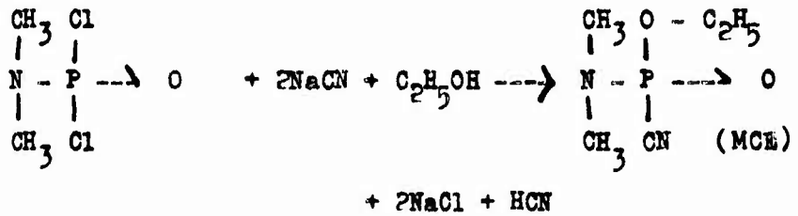
or 

Step 

IV. EXPERIMENTAL.

A. Materials.

1. Benzene, C_6H_6 - Baker's C.P. grade

2. Chlorobenzene, C_6H_5Cl - E. I. du Pont de Nemours & Co., commercial grade

3. Dimethylamine, $(CH_3)_2NH$ - The Matheson Co., cylinder grade - East Rutherford, N. J.

4. Dimethylamine hydrochloride, $(CH_3)_2NH_2^+ Cl^-$ Eastman's, white label grade

5. Ethanol, absolute, C_2H_5OH - Commercial Solvent Corp., gold seal grade.

6. Phosphorus oxychloride, $POCl_3$ - Ohio Apex, Inc., Nitro, W. Va.

7. Sodium Cyanide, NaCN, - Mallinckrodt's Reagent grade.

Some of the physical characteristics of the $POCl_3$ used, as described in item 6 above, are given below. These analyses are included to aid in setting up the specification requirement for this raw material.

Boiling Range (ASTM D86-40)

ml.	Temp., °C
1st drop	105.5
5	106.7
10	106.9
20	107.0
30	107.1
40	107.3
50	107.5
60	107.3
70	107.2
80	107.4
90	107.5
95	107.8
99	114.0

Recovery = 99.0%

[redacted]

For $POCl_3$

	Calculated	Found
% Cl	69.36	69.97
% P	20.20	20.35

Density = 1.672 g./ml. at 25°C.

B. Procedure.

Inasmuch as the two-step process for making MCE (as described under "Theoretical", Section III, of this report) was studied under several variable conditions, each procedure is discussed separately in the next section, entitled "Results".

For the sake of convenience, the original German method, as outlined in Intelligence Division Report No. 3709, is given below. It is this method on which the work described in this report was based.

"81 g. (1 mol) of dimethylamine hydrochloride is heated (108-110°C.) under reflux for 4 to 5 hours with 600 g. (excess) of $POCl_3$. The salt is then in solution. Fractionation in vacuo yields 150 g. (theory = 162 g.) of dimethylaminophosphoric acid dichloride, boiling at 71°C. at 10 mm. Hg.

"81 g. (1 mol) of the preceding compound is dropped with stirring into a mixture of 90 ml. of C_6H_6, 70 g. of dry $NaCN$, and 25 g. of 99.8% ethanol. The temperature rises rapidly to 40°C. and is controlled at this point by cooling. Upon completion of the reaction, the reaction is held one more hour at 40°C. It is then filtered and fractionally distilled. Yield = 70-75 g. of dimethylamino cyano-phosphoric acid ethyl ester (this is MCE - authors) boiling at 93°C. at 2 mm. Hg."

C. Results.

1. Synthesis of the Intermediate, Dimethylaminodichlorophosphine Oxide.

a. Use of Dimethylamine Hydrochloride.

Four runs were made reacting dimethylamine hydrochloride in an excess of $POCl_3$ with the view of establishing the most favorable $POCl_3$-amine hydrochloride ratio.

One mol of the amine hydrochloride and 2 to 4 mols of $POCl_3$ were placed in a 500-ml., 3-neck round-bottom flask equipped with thermometer, stirrer, and reflux condenser terminating in a $CaCl_2$ trap. A "Glas-Col" electric heater served as heating unit for the reactor. After a reaction period of approximately 6 hours at about 110°C., the product was fractionally distilled. Table 1 gives the results obtained. The boiling points of the product are given as a function of pressure in figure 1 in the appendix of this report.

Table 1

Reaction Data on the Formation of Dimethylaminodichlorophosphine Oxide

Run No.	$POCl_3$ g.	$POCl_3$ mols	$(CH_3)_2NH_2Cl$ g.	$(CH_3)_2NH_2Cl$ mols	Ratio $POCl_3$/ Amine hydrochloride	Total Reaction Time. hr.	Max.Reaction Temp. °C.	Dis B.P. °C/mm
1	600.0	3.91	81.0	0.99	4.0	6.5	111	81/14
3	460.1	3.00	81.6	1.00	3.0	6	111.5	80/12
2	306.7	2.00	81.6	1.00	2.0	6	110	75/10 44/1
4	308.4	2.01	81.6	1.00	2.0	6	111	79-80/12

Table 1

hylaminodichlorophosphine Oxide from $POCl_3$ and Dimethylamine Hydrochloride

eaction . hr.	Max. Reaction Temp. °C.	Dimethylaminodichlorophosphine Oxide Obtained							Still Residue after distillation - g.
		B.P. °C/mm Hg	g.	Yield %	n_D^{20}	d 20/4	%Cl	%N	
.5	111	81/14	148.5	92.5	1.4630	1.363	43.84	8.60	3.8
	111.5	80/12	144.6	89.3	1.4650	1.363	43.64	8.36	8.1
	110	75/10 44/1	66.4	41.0	1.4640	1.365	44.01	8.55	4.5
	111	79-80/12	105.1	64.9	1.4640	1.360	43.91	8.50	5.5

[redacted]

A portion of the distillate from run 1 (table 1) was analyzed for carbon, hydrogen, and other elements yielding the following results:

For $C_2H_6ONPCl_2$	Calculated	Found
% C	14.83	14.86 ± 0.08
% H	3.73	3.74 ± 0.03
% Cl	43.78	43.76, 43.89
% N	8.65	8.59, 8.60
% P	19.13	not done

An idea of the time-temperature relationship during the reaction may be obtained from the data collected in run 2, table 1. This relationship, although cited only for run 2, was virtually identical in all runs where the amine hydrochloride was employed. The data are given in table 2.

Table 2

Time-Temperature Relationship for the
Reaction: $(CH_3)_2NH_2Cl + POCl_3 \longrightarrow (CH_3)_2N\text{-}POCl_2 + 2HCl$

Time hr: min.	Temp. of Reaction Medium °C.	
0: 00	25	
0: 11	52	
0: 19	74	← HCl gas begins to be evolved at this point
0: 22	82	
0: 27	86	
0: 31	92	
1: 05	99	
2: 20	100	
3: 10	100	
4: 00	105	
5: 08	106	
6: 00	110	

b. Use of Free Dimethylamine as a Benzene Solution.

At the present time gaseous dimethylamine is produced in the United States in relatively large amounts whereas the hydrochloride is quite scarce. Consequently, it seemed worthwhile to investigate the feasibility of using the more available of these two materials and at the same time to establish whether or not a $POCl_3$-amine ratio less than 3 to 1 is sufficient for high yields of the MCB intermediate when the free amine is employed in place of its hydrochloride. The data derived from this investigation are compiled in table 3.

The procedure used in this phase of the work was the following:

A desired quantity of $POCl_3$ was placed in a 500-ml. 3-neck round-bottom flask equipped with thermometer, stirrer, dropping funnel, and reflux condenser terminating in a $CaCl_2$ trap. From the dropping funnel a benzene solution of dimethylamine (previously prepared from benzene and the liquified amine) was added dropwise with slow stirring to the $POCl_3$. An immediate temperature rise of the contents of the flask was observed and the rate of the amine addition was adjusted such that the reaction temperature was about 60°C. In some instances external cooling by means of an ice-H_2O bath was applied to the reactor.

After all of the amine had been added, the stirring rate was increased slightly and simultaneously the reaction temperature was raised to the reflux temperature of benzene, about 90°C. It was found convenient, to install a small total reflux - partial take off still-head arrangement on the reaction flask. In this way, benzene could be removed from the reaction medium, thus making it possible to increase the reaction temperature to about 100-120°C.

The over-all effect of using the free amine in place of its hydrochloride can be expressed by the equations:

$$2(CH_3)_2NH + POCl_3 \longrightarrow (CH_3)_2N\text{-}\underset{\underset{O}{\downarrow}}{P}Cl_2 + (CH_3)_2NH_2^+\ Cl^-$$

$$(CH_3)_2NH_2^+\ Cl^- + POCl_3 \longrightarrow (CH_3)_2N\text{-}\underset{\underset{O}{\downarrow}}{P}Cl_2 + 2HCl$$

In other words, the second step is identical with the procedure in which the hydrochloride is used exclusively as described in section IV 1 a. Insufficient reaction time or an insufficient excess of $POCl_3$ therefore necessitates an additional filtration step to free the reaction product of unreacted dimethylamine hydrochloride prior to distillation of the MCE intermediate.

After the reaction was complete, the product was distilled in vacuo. The benzene and $POCl_3$ portions of the distillate were combined, weighed, and $POCl_3$ was determined in the mixture by means of a chlorine analysis, assuming, of course, that all of the chlorine present was due to $POCl_3$.

Dimethylaminodichlorophosphine oxide exhibits considerable thermal stability and can be conveniently distilled at almost any pressure below 100 mm. of Hg.

In runs 5 and 6 (table 3) the still residues amounting to 42.9 and 34.5% of the total reaction product respectively, were analyzed for their chlorine contents. These amounted to 20.94 and 20.56%, respectively, for runs 5 and 6. It is interesting to note that the double-substitution product between dimethylamine and $POCl_3$, namely bis-dimethylaminochlorophosphineoxide, $(CH_3)_2N\text{-}\underset{\underset{O}{\downarrow}}{P}(Cl)\text{-}N(CH_3)_2$

Table 3

Reaction Data on the Formation of Dimethylaminodichlorophosphine Oxide from $POCl_3$ and Dimethylamine in the Presence of Benzene

Run No.	$POCl_3$ g.	$POCl_3$ mols	$(CH_3)_2NH$ g.	$(CH_3)_2NH$ mols	Ratio $POCl_3$/amine	C_6H_6 ml	addition time of C_6H_6-amine mixture & temp. min/°C.	Total reaction time after amine addition hr.	Max. Reaction Temperature °C.	Benzene distilled off during reaction ml.	Dimethylamine hydrochloride filtered off before distilling g.(approx.)	P.P. °C/mm Hg	Yield g.	Yield %	n_D^{20}	d 25/4	% Cl	Still residue after distilling g.	Still residue after distilling % of total product	$POCl_3$ - C_6H_6 fraction after stripping g.	$POCl_3$ - C_6H_6 fraction after stripping % Cl	Extracted $POCl_3$ found (by Cl) Total chlorine as $POCl_3$ g.	Extracted $POCl_3$ found (by Cl) $POCl_3$ mols
5	76.7	0.50	28.8	0.55	0.94	90	70/25-42	0.5	29-42	0	-	43-53/1.2-2.1	15.6	19.8	1.4625	1.346	43.69	11.7	42.9	146.2	15.95	28.29	0.22
6	"	"	"	"	"	"	55/28-53	"	50-55	0	31.5	44.5-[illegible]/1.5-2.1	20.5	75.5	1.4620	1.351	45.52	10.8	54.5	226.2	17.76	40.17	0.35
7	"	"	"	"	"	"	59/40-49	1.0	88-90	0	26.4	45-47.5/1.5-2.1	29.9	36.3	1.4620	1.365	45.59	8.5	72.2	158.9	15.42	22.73	0.22
14	"	"	"	"	"	"	35/51-58	5.0	87-89	0	24.7	41-47/1-1.5	39.8	49.1	1.4619	1.364	45.62	10.0	20.1	146.1	11.54	16.86	0.16
9	"	"	45.1	1.00	0.50	"	80/56-69	1.0	92-94	0	60.1	42-47/1-1.5	40.4	49.9	1.4621	1.365	45.66	21.0	34.2	99.4	3.04	3.02	0.08
8	"	"	23.9	0.53	0.94	"	84/45-48	"	87	0	56.0	41-45.5/1-1.5	28.0	34.6	1.4618	1.365	45.62	7.2	20.5	146.2	15.97	23.20	0.22
10	"	"	67.6	1.50	0.55	"	90/63-82	"	88-101	0	107.0	41-47/1-1.5	32.2	39.8	1.4619	1.362	45.58	36.8	53.3	158.3	0.23	0.36	0.008
11	115.1	0.75	22.5	0.50	1.50	"	80/53-57	6.0	87-95	0	-	47-51/2.1	65.1	80.4	1.4619	1.365	45.95	6.7	9.3	182.3	1.68	2.79	0.08
12	"	"	"	"	"	"	51/50-60	5.0	88-119	s2(1)	0	52/2.5-8	72.6	88.6	1.4620	1.364	44.07	4.4	5.7	102.7	25.30	34.79	0.55
13	"	"	"	"	"	"	41/56-61	4.0	90-116	s1(2)	0	54-64.5/6	70.1(3)	86.5	1.4625	1.364	45.98	4.0	5.4	108.2	25.75	33.71	0.52
15	460.1	3.00	45.8	1.02	2.94	"	48/60-61	6.0	97-114	s0(4)	0	50.5-52.5/2.5	142.6(3)	88.5	1.4655	1.364	43.96	9.4	6.2	366.5	57.09	250.00	2.16
16	308.7	2.00	45.1	1.00	2.00	"	60/60-64	"	97-118	s0(5)	0	56.5-57.5/3.5-4	141.0(3)	87.1	1.4621	1.365	43.33	9.4	6.5	219.4	48.43	124.92	1.17

(1) contained 12.7 g. $POCl_3$
(2) " 10.5 " "
(3) also analyzed after stripping free of $POCl_3$ and before distillation
(4) contained 30.1 g. $POCl_3$
(5) " 26.9 " "

[redacted]

requires 20.79% chlorine.

In addition to analyzing all of the runs listed in table 3 by vacuum distillation, the products of three runs were analyzed prior to vacuum distillation, that is to say, after all of the benzene and $POCl_3$ had been stripped off. The results of these analyses are given in table 4.

Table 4

Analyses of Stripped MCE Intermediate prior to Vacuum Distillation

Run No.	n_D^{20}	d 25/4	Cl* - %
13	1.4639	1.365	42.66
15	1.4650	1.364	42.43
16	1.4655	1.365	42.18

* Theoretical Cl = 43.78% - for other data pertaining to these runs, see table 3.

c. Use of Gaseous Dimethylamine.

It was shown in the previous section that a benzene solution of dimethylamine could be substituted for dimethylamine hydrochloride in the condensation with $POCl_3$ to form the MCE intermediate. The results also indicate that the molar ratio of $POCl_3$-amine required for high yields of the MCE intermediate is less than the molar ratio required in those runs where the amine hydrochloride is used.

From the standpoint of economy, it appeared advisable to eliminate the use of the carrier solvent, benzene. Accordingly, two runs were made in which the free amine was allowed to vaporize into an excess of $POCl_3$. The apparatus was identical with that described in the previous section except for the fact that the dropping funnel was removed and replaced by a gas inlet tube reaching to within about one inch above the $POCl_3$ surface. The gas inlet tube was connected to a small flask containing the required amount of liquified dimethylamine. By external control of the temperature of the amine reservoir, the flow rate of gaseous amine could easily be adjusted. The reaction data pertaining to these runs are given in table 5.

As done previously, the reaction products were analyzed by vacuum distillation.

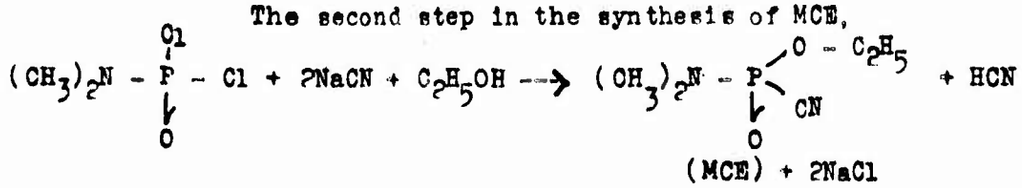
Table 5

Reaction Data in the Formation of Dimethyl[illegible]odichlorophosphine Oxide from $POCl_3$ and Gaseous Dimethylamine

	Run 18	Run 19
$POCl_3$ - grams	345.0	680.9
$POCl_3$ - mols	2.25	4.44
$(CH_3)_2NH$ - grams	33.8	100.0
$(CH_3)_2NH$ - mols	0.75	2.22
Ratio - $POCl_3/(CH_3)_2NH$	3.0	2.0
Addition time of amine - min./°C.	17/25-75	44/25-74
Reaction time after amine addition - hr.	6	6
Maximum reaction temp. °C.	105-119	116-121
Unreacted recovered $POCl_3$ - grams	239.7	354.5
Analysis of stripped intermediate		
n_D^{20}	1.4638	1.4646
d 25/4	1.364	1.366
% Cl	42.82	42.87
Analysis of distilled intermediate		
boiling point °C./mm. Hg.	38.5-39.5/1.5	37.5-39.5/1
yield - grams	101.6	323.9
yield - %	83.6	90.1
n_D^{20}	1.4627	1.4620
d 25/4	1.364	1.363
% Cl	43.83	43.76
still residue, grams	3.9	11.0
still residue, % of total product	3.7	3.3

2. Synthesis of MCE.

The second step in the synthesis of MCE,



$$(CH_3)_2N-P(=O)(Cl)-Cl + 2NaCN + C_2H_5OH \rightarrow (CH_3)_2N-P(=O)(O-C_2H_5)(CN) + HCN$$

(MCE) + 2NaCl

was investigated under several conditions which follow.

a. Runs According to Described German Method.

Under section IV B, the German method for the synthesis of MCE from dimethylaminodichlorophosphine oxide was described in detail. Six runs were made using this method. The results obtained are given in table 6.

As learned later, the clue to a successful synthesis of MCE from the intermediate, NaCN, and ethanol is the absence of all water and protection of the reaction vessel from atmospheric moisture.

The presence of moisture will not only hydrolyze MCE directly but also the dichloro intermediate with the liberation of HCl. This liberation of HCl will then in turn cause the decomposition of MCE.

In one experiment dry gaseous HCl was allowed to come in contact with dry MCE*. A test for dimethylamine was at once positive, indicating the rupture of the MCE molecule at the nitrogen-phosphorus linkage. It follows from these facts that an excess of NaCN is essential in the process to assure the decomposition of HCl,

$$NaCN + HCl \longrightarrow NaCl + HCN$$

and thus to remove active ionic hydrogen from the reaction medium.

An examination of the data reveals that the percentage yields in runs A and D are perceptibly lower than in other runs. These discrepancies are accounted for in the following way.

In run A, the crude MCE reaction product was distilled in a 24-inch Penn State Column of about 1 inch diameter, filled with 1/8-inch glass helices. This type of column requires a high kettle temperature and this is believed to cause considerable thermal decomposition of MCE. Consequently, in all of the other runs listed in table 6, the 24-inch column was replaced by a 6-inch column of 1-inch diameter filled with 6-mm. solid glass beads. An examination of figure 1, in the appendix of this report, where the boiling points of $POCl_3$, the intermediate, and MCE are plotted, shows that in actual practice a column equivalent to only a few theoretical plates (about 3) should be sufficient for reasonably good separation of the products.

In run D, the low yield of MCE must be attributed to the moisture content of the reagents. At the time of the synthesis described in run D, the atmospheric humidity at Edgewood Arsenal was unusually high. No special precautions had been taken to dry all of the reagents and as noted under "Remarks" in run D (table 6), the ethanol used was found to contain more than 1% of H_2O. It was found convenient to dry the reagents, benzene or chlorobenzene and NaCN mixture, by heating with stirring and reflux. Under these conditions, water and benzene or chlorobenzene will distill off an azeotropic mixture. If initially an excess of benzene or chlorobenzene

*This test was made by Dr. Benjamin Witten of the Chem. Div. CWS Technical Command, Edgewood Arsenal, Md.

Run No.	Benzene or chlorobenzene ml.	NaCN(1) g.	mols	C_2H_5OH(1) g.	mols	Dimethylaminodichlorophosphine Oxide Sample used	g.	mols	Addition time-min	Reaction time under own heat of reaction at 40°C - min	Heating period at 40°C after own heat of reaction subsided-min	B.P. °C/mm Hg
A	90 benzene	70.0	1.42	25.0	0.54	Run 1 Table 1	81.0	0.50	70	10	60	72.5-73 ca 1.5
B	"	"	"	"	"	run 3 Table 1	"	"	45	34	"	86-87 3
C	90 chlorobenzene	"	"	"	"	Run 4 Table 1	"	"	39	40	"	73-75 ca 1.8
D	90 benzene	"	"	"	"	see remarks	"	"	43	142	"	79-83 2
E	90 benzene	"	"	"	"	same as run D	"	"	44	45	45	79-83 2-2.5
H	90 chlorobenzene	"	"	"	"	"	"	"	43	79	90	80-83 2.5

(1) The quantities used were those recommended.

Table 6

Synthesis of MCE

Reaction Temperature = 40°C.

Reaction time under own heat of reaction at 40°C - min	Heating period at 40°C after own heat of reaction subsided-min	MCE Obtained upon distillation - main cut								Distillation Foreshot to main cut	
		B.P. °C/mm Hg	Yield g.	Yield %	n_D^{20}	d 20/4	Chlorine content %	N Content %	Active CN %	g.	n_D^{20}
10	60	72.5-75 / ca 1.5	39.8	49.1	1.4240	1.080	trace max.= 0.04	17.05	15.62	0.5	1.446
34	"	86-87 / 3	60.5	74.6	1.4236	1.076	0.39	"	15.55	-	-
40	"	73-75 / ca 1.8	59.1	72.9	1.4243	1.078	0.56	16.91	15.30	0.3	1.448
142	"	79-83 / 2	43.8	54.0	1.4240	1.079 at 25/4	0.66	16.80	15.62	ca 1	1.431
45	45	79-83 / 2-2.5	64.5	79.6	1.4257	1.086 25/4	1.82	16.70	15.87	2.7	1.45
79	90	80-83 / 2.5	65.7	81.1	1.4243	1.082 25/4	0.92	-	15.63	-	-

uantities used were those recommended in I.D.R. No. 37

e	N Content %	Active CN %	Distillation Foreshot to main cut g.	n_D^{20}	Distillation Residue g.	Remarks
	17.05	15.62	0.5	1.4463	about 20	-
	"	15.55	-	-	4.6	-
	16.91	15.30	0.3	1.4480	7.4	-
	16.80	15.62	ca 1	1.4319	18.7	1. Benzene and NaCN dried by refluxing and H_2O removal as azeotrope 2. Intermediate used was redistilled composite of several samples. b.p. = 120°C/77 mm Hg, n_D^{20} = 1.4620, d 25/4 = 1.363 3. Ethanol used contained 1.02% H_2O by Karl Fischer reagent
	16.70	15.87	2.7	1.4501	4.5	1. Ethanol dried over $CaSO_4$ before use - contained about 0.5% H_2O by Karl Fischer reagent 2. Benzene and NaCN dried by refluxing and H_2O removed as azeotrope
	-	15.63	-	-	6.7	Same as run E, except that chlorobenzene was used in place of benzene

(ca 120-150 ml.) is used in place of the required 90 ml., the removal of 30-60 ml. of benzene or chlorobenzene by distillation from its mixture with NaCN will sufficiently dry the reagents. In the laboratory, the ethanol used was dehydrated over "Anhydrone" ($CaSO_4$) prior to its addition to the already dried NaCN - benzene mixture. It is believed that azeotropic drying is applicable to plant operations and in all probability can be extended to the benzene-ethanol-NaCN system simultaneously, thus eliminating the separate drying of ethanol as described above.

The distilled reaction product from run A was subjected to a carbon and hydrogen analysis. The results follow.

For $C_5H_{11}O_2PN_2$	Calculated	Found
% C	37.02	36.8 ± 0.1
% H	6.84	6.99 ± 0.02

It has been stated that the dropwise addition of the intermediate, dimethylaminodichlorophosphine oxide, to the benzene-ethanol-NaCN mixture gives rise to a rather exothermic reaction. In table 7, the time-temperature data, together with the addition rate of the intermediate, are given for runs B, C, and D (table 6).

Table 7

Time-Temperature Relationship in Synthesis of MCE

Time min.	Run B	Run C	Run D*
0	25.5	28.0	29.0
1	28.0	31.5	-
2	31.0	37.0	-
3	35.0	40.0	-
4	40.0	-	31.0
12	-	-	40.0
Average addition rate of intermediate g./min.	1.80	2.08	1.88

* contained moisture - see table 6 and text.

As outlined before, the crude reaction product is filtered free of inorganic salts just before distillation of the product. An examination as to the phosphorus content of two filter cakes was made (runs D and H, table 6)). The phosphorus content so found was taken to be due to occluded or adsorbed MCE. In run D, for example, the phosphorus content of the filter cake amounted to 6.1% immediately after the reaction product had been completely filtered. Washing this same filter cake with 50 ml. of benzene reduced the phosphorus content to 0.9%. It should be pointed out here that the

filtration should be made as rapidly as possible to prevent prolonged exposure of the product to moisture. In run F, filter-aid "Celite 503" was used in the filtration of the product and after washing with 100 ml. of chlorobenzene the phosphorus content of the filter cake (not containing filter-aid) amounted to 0.6%. Calculated as MCE, these values of 0.9 and 0.6% of P correspond to 4.7 and 3.1% of MCE, respectively, and show that the filter cake in all probability must be decontaminated (aqueous caustic) before disposal.

b. Investigation on Stripped, Undistilled MCE. (Run F, not shown in table 6).

In view of the high boiling point of MCE and its sensitivity toward thermal decomposition, both of which factors could be the source of difficulties in plant operations, an investigation was made on the nature of the MCE residue after stripping off excess solvent in vacuo. Accordingly, the following run was made:

79 g. of NaCN and 120 ml. of benzene was refluxed and 30 ml. of benzene containing about 0.3 g. of water was removed as an azeotropic mixture. 25 g. of previously dried ethanol was added to the reaction mixture. From the dropping funnel 81 g. of freshly distilled MCE intermediate was added dropwise over a period of 118 minutes, keeping the reaction temperature at 40°C. After all of the intermediate had been added, the reaction mixture was stirred at 40°C. for one hour.

After filtering off inorganic salts, the filtrate was subjected to partial vacuum stripping at 140-150 mm. Hg. pressure and the still residue was again filtered to remove some inorganic salts which had settled out during the stripping operation. After filtering, there was obtained 84.1 g. of partially stripped undistilled MCE, having the following analysis:

Color = amber but clear

$n_D^{20} = 1.4291$

d 25/4 = 1.082
% Cl total = 1.42
% Cl hydrolyzable = 1.41
% CN = 11.50
% N = 13.35
% P = 15.38

Assuming that all of the hydrolyzable chlorine present is due to the MCE intermediate, and adjusting the nitrogen and phosphorus analytical data accordingly, the results given in table 8 are obtained.

Table 8

Calculations of Yield and Purity on Run F
Wt. of product = 84.1 g.

Content of Unreacted MCE Intermediate

% Hydrolyzable Cl = 1.41

Theoretical Cl content of intermediate, % = 43.78

Chlorine content in sample as % intermediate = $\frac{1.41}{43.78} \times 100 = 3.22$

Adjustment of N and P Results

Theoretical N content of intermediate, % 8.65

% N per % Cl in intermediate = $\frac{8.65}{43.78}$ = 0.1976

% N required for 1.41% Cl		0.28
Adjusted % N = 13.35 (total)	− 0.28 (intermediate)	13.07 (MCE)

Theoretical P content of intermediate, %		19.13
% P per % Cl in intermediate	$=\frac{19.13}{43.78}$	0.4370
% P required for 1.41% Cl		0.62
Adjusted % P = 15.38 (total)	− 0.62 (intermediate)	14.76 (MCE)

Calculation of MCE Content - % Purity

% active CN found = 11.50

% Purity by CN = $\frac{11.50}{16.05} \times 100 = 71.65$

% N as MCE = 13.07

% Purity by N = $\frac{13.07}{17.28} \times 100 = 75.64$

% P as MCE = 14.76

% Purity by P = $\frac{14.76}{19.11} \times 100 = 77.24$

Average Purity, % 74.84

Calculation of yield of MCE (theoretical yield = 81.07 g.)

From CN = 84.1 x 0.717 = 60.3 g.
= 74.4% of theory

From N = 84.1 x 0.756 = 63.6 g.
= 78.5 % of theory

From P = 84.1 x 0.772 = 64.9 g.
= 80.1% of theory

Average of yields as calculated above = 77.7% of theory

The average purity of the stripped sample, 74.84%, as calculated from table 8 and the percentage content of the intermediate, 3.22%, account for only 62.9 + 2.7 = 65.6 g. of the total product weight. Consequently, 84.1 - 65.6 = 18.5 g. of inert materials, chiefly benzene, were present in the stripped product, making the approximate composition of the product the following:

MCE	74.8%
MCE intermediate	3.2%
Benzene and other inert materials	22.0%

Similar data on stripped MCE prepared in chlorobenzene instead of benzene were obtained from a run already referred to in a previous section (run H, table 6). One interesting result derived from the analyses of the crude products of run H was the determination of the amount of HCN dissolved in the filtered reaction product. Immediately after filtration of the reaction product from run H (prepared as described under section IV C ? a), the filtrate was analyzed for % active CN. The filtrate was then subjected to vacuum distillation, partially stripped free of chlorobenzene, and again analyzed for % active CN. During the first stages of stripping, considerable gas evolution occurred which was found to be the escape of dissolved HCN in the reaction product. The presence of dissolved HCN in the crude reaction product, prior to the application of vacuum is, of course, common to all MCE runs. The data obtained from run H are recorded in table 9.

Table 9

Analyses of Stripped MCE, prepared in Chlorobenzene (Run H, table 6)

Before stripping	
Weight of filtrate immediately after reaction	235.4 g.
CN content of filtrate	7.71%
Weight of total CN present in filtrate	18.15 g.
After stripping at 54 mm. Hg	
Weight of stripped residue	165.3 g.
CN content of residue	6.71%
Weight of CN in residue	11.09 g.
Amount of HCN present in original filtrate	
CN removed after application of vacuum	7.00 g.
CN removed, calculated as HCN	7.33 g.
HCN in original filtrate	3.11%
Calculation of yield	
CN in stripped residue	6.71%
Theoretical CN in MCE	16.05%
MCE in stripped residue by CN	41.81%
	69.2 g.
Yield = $\frac{69.2}{81.07} \times 100$	85.2% of theory
Yield by distillation (see table 6)	65.7 g.
Distillation residue	6.7 g.

c. Preparation of MCE Using Stripped, Undistilled Intermediate (Run G, not shown in table 6).

As shown in runs F and H, the final step in the MCE synthesis does not demand a distillation. Furthermore, a distillation of MCE on plant scale is highly impractical. It remains to be shown now whether or not a stripped rather than a distilled sample of dimethylaminodichlorophosphine oxide may be used as intermediate in the synthesis of MCE as outlined for run F. If so, then the entire synthesis of MCE from its principal raw materials, dimethylamine, $POCl_3$, ethanol, and NaCN, can be accomplished without any distillation.

It is in this connection that chlorobenzene shows properties superior to benzene. The boiling point of chlorobenzene (132.1°C.) is higher than that of $POCl_3$ (107.3°C.). This means that the addition of chlorobenzene to the reaction product of the first step in the MCE synthesis assures the removal of all $POCl_3$ from the stripped dimethylaminodichlorophosphine oxide.

A glance at figure 1 in the appendix of this report will clarify this point. An identical mode of procedure has been suggested by Dr. Kharasch in a letter to Gen. Kabrich, Commanding General, CWS Technical Command, Edgewood Arsenal, Md.

The stripped MCE intermediate containing some chlorobenzene, if desired, can now be reacted with a mixture of NaCN, ethanol, and chlorobenzene, as already described.

The description of run G follows:

40.8 g. (0.5 mol) of dimethylamine hydrochloride and 230.0 g. (1.5 mol) of $POCl_3$ were heated at 95-112°C. for 6 hours. At the end of the reaction period, the product was stripped in vacuo at 47°C./91 mm. Hg. until most of the $POCl_3$ had been stripped off. The distillation was interrupted and 50 ml. of chlorobenzene was added to the still pot contents. Stripping was continued until most of the chlorobenzene had been removed from the still pot. There remained 79.0 g. of stripped MCE intermediate with the following analysis:

	Calculated	Found
% N	8.65	8.66
% P	19.13	19.09
% Cl, total	42.24	-
% Cl, hydrolyzable	41.80	43.78
% Cl, as chlorobenzene (by difference)	0.44	-

64.6 g. of the dimethylaminodichlorophosphine oxide, so prepared, was added dropwise in 40 minutes to an anhydrous mixture of 70 g. of NaCN and 25 g. of dry ethanol in 90 ml. of chlorobenzene. After a reaction

period of 2 hours, the product was filtered, the filter cake washed with 100 ml. of chlorobenzene, and the filtrate subjected to vacuum stripping at 64.5°C/81 mm. Hg. When practically all of the chlorobenzene had been removed, the still residue was again filtered to remove a small amount of insoluble material which had settled out during the stripping operation. This filter cake was rinsed with 27 ml. of chlorobenzene and these rinsings were added to the reaction product. There remained 69.2 g. of partially stripped MCE having the following analysis:

n_D^{20} = 1.4616
d 25/4 = 1.096
active CN = 8.85%
N = 9.94%
P = 11.26
total Cl = 12.88%
hydrolyzable Cl = 0.40%
Cl, as chlorobenzene, by difference = 12.48%

The calculations pertaining to run G have been compiled in table 10.

Table 10

Analysis of Stripped MCE Prepared from the Undistilled Intermediate
(Run G)

Content of unreacted MCE intermediate	
% hydrolyzable Cl	0.04
Theoretical Cl content of intermediate, %	43.78
Cl content in sample as % intermediate	0.09
Adjustment of N and P Contents	
Theoretical N content of intermediate, %	8.65
% N per % Cl in intermediate	0.1976
% N required for 0.04% Cl	0.08
Adjusted % N = 9.94 (total) − 0.08 (intermediate)	9.86 (MCE)
Theoretical P content of intermediate, %	19.13
% P per % Cl in intermediate	0.4370
% P required for 0.04% Cl	0.17
Adjusted % P = 11.26 (total) − 0.17 (intermediate)	11.09 (MCE)
Calculation of MCE content - % Purity	
% active CN found	8.85
% Purity by CN	55.14

% N as MCE	9.86
% Purity by N	57.06
% P as MCE	11.09
% Purity by P	58.03
Average purity	56.74

Calculation of yield of MCE (theoretical yield = 64.7 g.)

From CN = 35.7 g. = 55.2% of theory

From N = 36.9 g. = 57.0% of theory

From P = 37.5 g. = 58.1% of theory

Average of yields as calculated above = 56.8% of theory

From the calculations listed in table 10, the approximate composition of the stripped MCE is found to be:

Unreacted intermediate = 0.1%	
Chlorobenzene and other impurities, by difference	43.2%
MCE	56.7%
Chlorobenzene, from non-hydrolyzable Cl content	39.6%
impurities, by difference	3.6%

V. DISCUSSION.

Inasmuch as the results have already been discussed in some detail in the foregoing section, repitition will be avoided.

Reviewing the two-step synthesis of MCE as a whole, several factors should be considered particularly from the standpoint of plant-scale operations. These are,

1. Availability of raw materials
2. Economics of process
3. Most favorable reaction conditions, and
4. Most favorable procedure for best yields and highest quality of MCE

Gaseous dimethylamine is available in this country and readily procured. Run 12 (table 3) as well as run 19 (table 5) show that molar ratios of $POCl_3$ to the amine of 1.5 and 2.0 produce 89.6 and 90.1% yields of dimethylaminodichlorophosphine oxide, respectively. Using dimethylamine hydrochloride, in place of the free amine a $POCl_3$ to amine hydrochloride molar ratio of at least 3.0 is required for a similar yield (see run 3, table 1). Furthermore, the hygroscopic nature of dimethylamine hydrochloride makes its storage and handling difficult. A comparison between tables 3 and 5 also reveals the fact that the use of benzene as carrier solvent for the free amine is hardly necessary.

Since MCE exhibits thermal instability, a distillation of this material in plant procedure is undesirable. The MCE product can simply be stripped free of all volatile matter to any desired concentration in either benzene or chlorobenzene. In view of the required stripping operation for MCE, it is believed highly advisable to distill the MCE intermediate (dimethylaminodichlorophosphine oxide) prior to its reaction with NaCN and C_2H_5OH. If no distillation for the intermediate is included in the process, the residues and side products will be unnecessarily increased in the final product. One other added disadvantage to the use of undistilled intermediate, is that lower yields of MCE are obtained in the second step. This can be seen by comparing run G with run F and H.

The distillation of the MCE intermediate in moderate vacuo (80-100 mm. Hg.) has been repeatedly performed in the laboratory and is believed to be applicable to pilot-plant procedures.

The necessity of having dry reagents in the second step of the MCE synthesis strongly suggests the application of azeotropic distillation of the benzene (or chlorobenzene) - ethanol - NaCN system prior to the addition of the MCE intermediate. The reagents must be dry to obtain high yields of MCE, and every precaution must be taken in this direction. Data on azeotropic systems such as benzene-ethanol-water may be obtained from the published chemical literature.

VI. CONCLUSIONS.

1. Dimethylaminodichlorophosphine oxide can be prepared in yields of about 90% from $POCl_3$ and either dimethylamine hydrochloride or the free dimethylamine.

2. The use of the free amine in the synthesis of dimethylaminodichlorophosphine oxide requires only 1.5 to 2 mols of $POCl_3$ per mol of amine, whereas dimethylamine hydrochloride requires at least 3 mols of $POCl_3$ per mol of amine hydrochloride for comparable yields.

3. Under anhydrous conditions, the MCE intermediate will react with NaCN and ethanol in either benzene or chlorobenzene to produce about 80% of distilled MCE.

4. If distilled intermediate is used, merely stripping the MCE crude reaction products free of volatile matter will produce an acceptable grade of MCE in yields of about 78%.

5. Undistilled, stripped MCE intermediate can be used in the MCE synthesis, resulting, however, in somewhat lower yields and a product of inferior quality.

VII. RECOMMENDATIONS.

It is recommended that:

1. In pilot plant operations, dimethylaminodichlorophosphine oxide (MCE intermediate) be prepared by the direct action of 1 mol of gaseous dimethylamine on 1.5 to 2 mols of $POCl_3$.

2. The MCE intermediate be distilled before its reaction with the other reagents to produce MCE i undertaken.

3. In view of the sensitivity of the MCE synthesis toward moisture and HCl all reagents be kept thoroughly anhydrous. The azeotropic removal of water with benzene or chlorobenzene (or with ethanol and benzene) is recommended prior to the addition of the MCE intermediate to the other reagents.

FIGURE 1

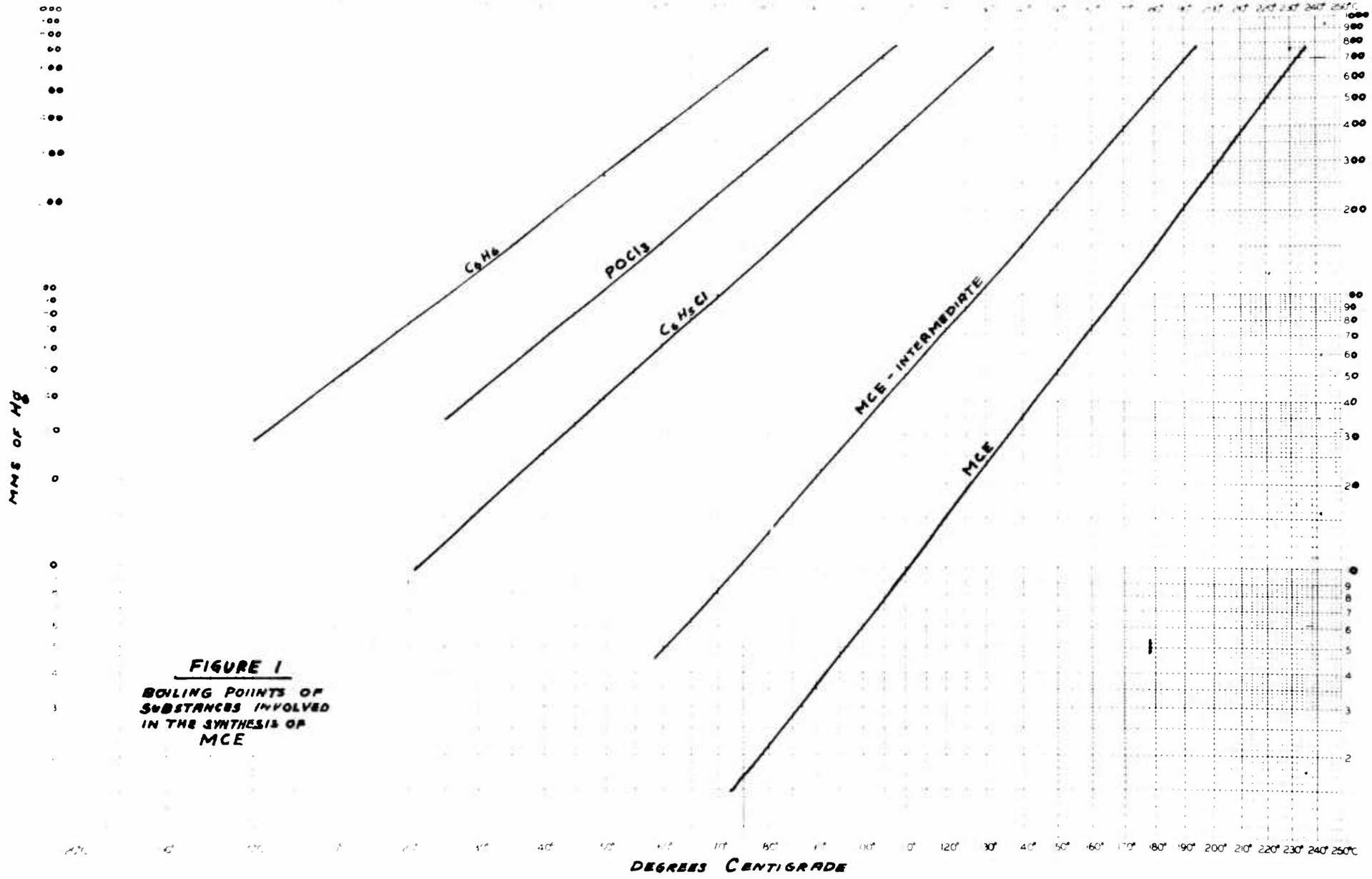


FIGURE 1

BOILING POIINTS OF SUBSTANCES INVOLVED IN THE SYNTHESIS OF MCE

T.D.M.R. 1138

Project: A 1.13

The Synthesis of MCE, Cyano dimethylamino) ethoxyphosphine Oxide.

Notebook No. 2384

Experimental work:
Started: 5-19-45
Completed: 8-10-45
(intermittent)

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REPLY TO
ATTENTION OF

RDCB-DPC-RS

FEB 18 2016

MEMORANDUM THRU Director, Edgewood Chemical Biological Center, (RDCB-D/Dr. Joseph L. Corriveau), 5183 Blackhawk Road, Aberdeen Proving Ground, Maryland 21010-5424

FOR Defense Technical Information Center (DTIC), 8725 John J. Kingman Road, Ft Belvoir, VA 22060-6218

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Encl

RONALD L. STAFFORD
Security Manager

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